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C−F Bond Cleavage and Unexpected C−CN Activation by Cobalt Compounds Supported with Phosphine Ligands

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Summary: A cyclometalation reaction involving C−F bond activation at a cobalt(I) center with an aldazine-N atom as an anchoring group, for the first time, affords an ortho-chelated cobalt(III) complex, ***1****, containing a [C−Co−F] fragment. Under otherwise similar conditions, the first example of an organo cobalt(II) cyanide,* ***2****, formed through Ar−CN bond activation could be obtained using the reaction of 2,6-difluorobenzonitrile with a cobalt(0) complex without C−F bond activation. Both* ***1*** *and* ***2*** *were characterized through X-ray diffraction.*

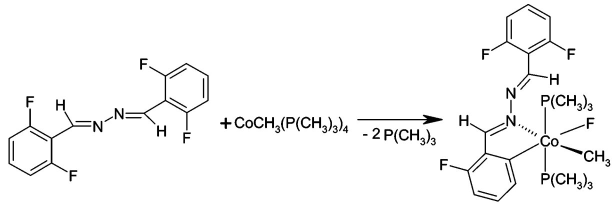
The activation of carbon−fluorine bonds is of great importance in organometallic chemistry and catalyst development because this type of reaction contributes to the fundamental understanding of the reactivity of stable bonds and the selective replacement of F atoms.[1−4] Reports on C−F activation by first-row transition metals are rare,[5] and no examples of organoiron or cobalt fluorides containing a C−M−F moiety have been described. The only cobalt-promoted carbon−fluorine bond activation was reported with ionic cobaltocenium fluoride as fluoride source.[6] Although C−F activation can be promoted by $Fe_2(CO)_9$ with *ortho*-halogenated aromatic aldazine ligands, no intermediate containing a C−Fe−F bonded fragment could be isolated.[7]

Interest in azine and diazine compounds either for pharmaceuticals or as building blocks for various applications with materials and in supramolecular chemistry has led to a variety of experimental and theoretical studies.[5c,8] Cleavage of the N−N bond in azines by transition metal complexes has been occasionally observed.[9,10]

Activation of nitriles is a very important issue in organometallic chemistry. Cleavage of C−CN bonds can be promoted by low-valent nickel complexes.[11] Miller reported an efficient cross-coupling of Grignard reagents with aryl nitrile derivatives affording the corresponding aryl alkanes or aryl alkenes through nickel-catalyzed breaking of the C−CN bond.[11b] Derivatives of pyridine can be selectively obtained by photochemical synthesis in cobalt(I)-catalyzed cocyclization of alkynes with nitriles.[12] However, in none of these reports was an Ar−M−CN intermediate isolated.

Cyclometalation reactions of substrates containing an imine or a pyridyl anchoring group by iron and cobalt complexes proceed through intramolecular C−H activation.[13]

We have recently observed a cyclometalation reaction involving carbon−fluorine bond activation at a cobalt(I) center with azine as an anchoring group, which, for the first time, affords an *ortho*-chelated cobalt(III) complex containing a C−Co−F fragment (eq 1).



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Upon combining the *ortho*-fluorinated aromatic aldazine ligand *N,N′*-bis-(2,6-difluorobenzylidene)hydrazone with methyl

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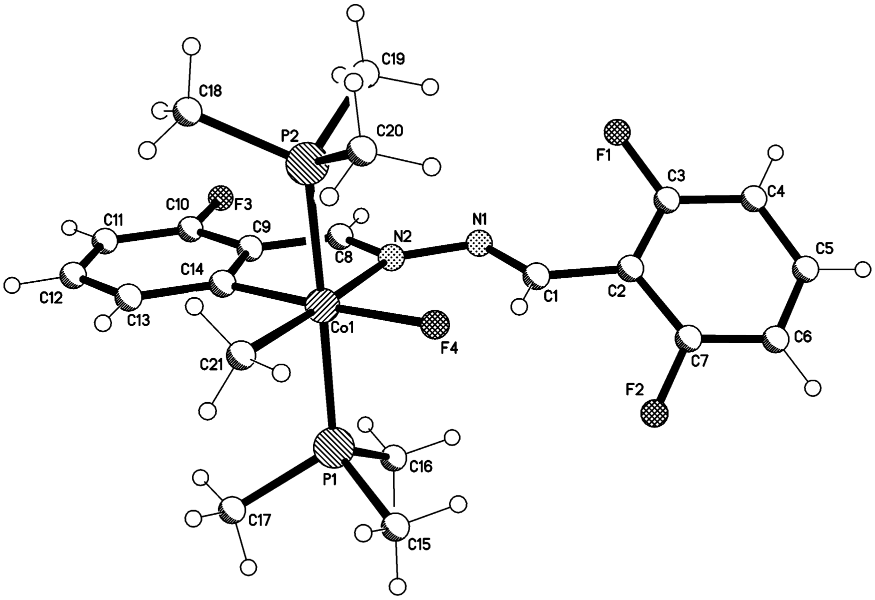


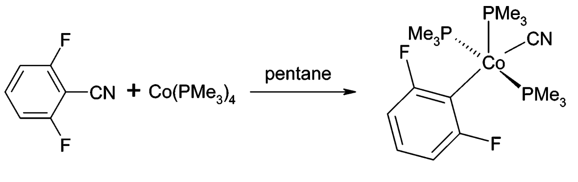
Figure 1. X-ray crystal structure of **1**. Selected bond distances (Å) and angles (deg): Co1−C14 1.907(2), Co1−F4, 1.941(1), Co1−C21 1.993(3), Co1−N2 2.048(2), Co1−P2 2.2082(8), Co1−P1 2.2145(8), N1−C1 1.260(3), N1−N2 1.414(3), N2−C8 1.293(8), C1−C2 1.468(3), C8−C9 1.423(3), C14−Co1−F4 176.62(8), C14−Co1−C21 94.3(1), F4−Co1−C21 88.92(9), C14−Co1−N2 82.35(8), F4−Co1−N2 94.41(7), C21−Co1−N2 176.65(9), C14−Co1−P2 91.15(7), C14−Co1−P1 92.19(7), F4−Co1−P2 88.04(5), F4−Co1−P1 88.96(5), C21−Co1−P2 86.7(1), N2−Co1−P2 92.95(6), N2−Co1−P1 93.29(6), P2−Co1−P1 173.27(3). C21−Co1−P1 87.2(1).

tetrakis(trimethylphosphine)cobalt(I) at room temperature, a color change from orange to red-brown was observed, indicating reaction. After workup the mono-*ortho*-metalated cobalt(III) fluoride **1** was obtained in 44% yield. Surprisingly, no products arising from an initial cleavage of the N−N bond[7] were found, at variance with a similar cyclometalation of *N,N′*-bis(pentafluorobenzylidene)hydrazone with iron observed recently.[14] No spontaneous elimination of fluoromethane occurred.

Complex **1** was characterized by elemental analysis, IR and NMR spectroscopy, and an X-ray diffraction analysis. The uncoordinated *H*CN group ($\nu(\mathrm{C{=}N}) = 1607.1\ \mathrm{cm^{-1}}$) gives rise to a singlet at 9.11 ppm, while the coordinated *H*CN group ($\nu(\mathrm{C{=}N}) = 1622.5\ \mathrm{cm^{-1}}$) shows a doublet at 10.75 ppm ($^4J_{\mathrm{FH}} =$ 32 Hz). Spectroscopic data are compatible with an octahedral configuration around the cobalt atom consisting of a P−Co−P axis and equatorial coordination of C, C, F, and N donor atoms. The red crystals of **1** under argon decompose at 200 °C and at ambient temperature in air remain stable for 2 h.

The molecular structure of **1** (Figure 1) confirms the octahedral geometry around cobalt. The diazine ligand is coordinated by one of the azine-N atoms and an *ortho*-chelated C atom, forming a five-membered metallacycle where the sum of internal bond angles (540°) indicates planarity. The bite angle of the chelating ligand [C14−Co−N2 = 82.35(8)°] is larger than that found in related compounds.[15] The C=N bond length of the coordinated nitrogen, C8−N2 (1.293(3) Å), is longer than that of the free C=N, C1=N (1.260(3) Å), while C8−C9 (1.423(3) Å) is shorter than C1−C2 (1.468(3) Å), which could be due to back-donation from the cobalt atom into a ligand π^*-orbital and the considerable conjugation in the cobaltocycle. The phenyl ring attached to the uncoordinated C=N group is rotated out of the chelating plane; the dihedral angle formed between these planes is 43.6(1)°. Within the chelating ring the bond angles C9−C8−N2 (116.6(2)°) and C8−N2−N1 (111.01(7)°) are smaller than the corresponding bond angles N1−C1−C2 (120.3(2)°) and N2−N1−C1 (113.7(2)°) in the uncoordinated moiety. A similar metallocycle of iridium(I) was proposed as an intermediate in the cyclometalation of a pentafluorobenzaldehyde azine phosphorane.[15]

In view of the many coordination modes observed for a cyano group, its anchoring properties are hard to predict. To test a possible C−F bond activation in an *ortho*-fluorinated benzonitrile, pentane solutions of 2,6-difluorobenzonitrile and tetrakis(trimethylphosphine)cobalt(0) were combined and kept at room temperature for 18 h to afford red-brown crystals of **2** in 53% yield (eq 2).



(2)

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The C≡N stretching vibration is found at 2073 cm^{-1}, which is close to that of $\mathrm{Co(CN)_5}^{2-}$ species.[16] The molecular structure of **2** shows a distorted square pyramidal coordination of a cobalt(II) center with one P atom in apical position. This five-coordinate geometry is typical for cobalt(II) cyanide complexes, as are the paramagnetic properties of **2**.[17] Owing to a steric effect of the *ortho*-fluorinated phenyl ring, the angle C1−Co−P3 (108.13(8)°) is larger than 90°, leaving both the P3 atom and the C≡N bond in the same plane with the phenyl ring, which is perpendicular to the square coordination plane. Although the strongly electron-withdrawing F-substituents weaken the Ar−CN bond, no product of the expected C−F activation with C≡N as an anchoring group was found. To the best of our

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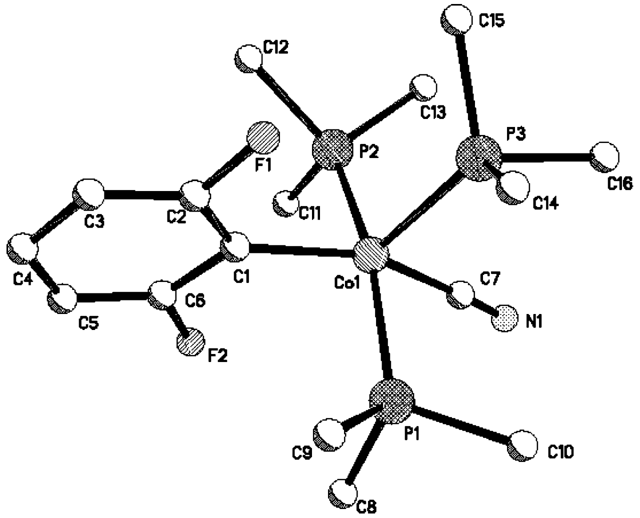

Figure 2. X-ray crystal structure of **2**. Selected bond distances (Å) and angles (deg): Co1−C7 1.922(3), Co1−C1,1.997(2), Co1−P1 2.2187(9), Co1−P2 2.2177(9), Co1−P3 2.3075(9), C7−N1 1.141(3), F1−C2 1.375(4), F2−C6 1.386(3); C7−Co1−C1 154.6(1), C7−Co1−P2 86.23(8), C1−Co1−P2 89.80(7), C7−Co1−P1 87.56(8), C1−Co1−P1 88.80(7), P2−Co1−P1 162.48(3), C7−Co1−P3 97.30(8), C1−Co1−P3 108.13(8), P2−Co1−P3 98.49(3), P1−Co1−P3 98.54(3).

knowledge, compound **2** is the first example of an organo cobalt(II) cyanide formed through Ar−CN bond activation. This type of metal complex has been synthesized through reaction of $M(PEt_3)_4$ (M = Ni, Pd, and Pt) with monofluorinated benzonitriles.[18] Organo nickel cyanides could be possible intermediates for cyanation[19] of aryl bromides and cross-coupling reaction of aryl halides.[11b] That the bond activation of Ar−CN suppresses C−F cleavage in fluorinated nitriles is verified by our work for cobalt.

Experimental Section

General Procedures and Materials. All air-sensitive and volatile materials were handled either in vacuo or under argon by using standard Schlenk techniques. Melting points/decomposition temperatures: sealed capillaries, uncorrected values. *N*,*N*′-Bis(2,6-difluorobenzylidene)hydrazine,[14] tetrakis(trimethylphosphine)cobalt(0), and methyltetrakis(trimethylphosphine)cobalt(I)[20] were prepared by published procedures. Other chemicals were used as purchased. All solvents were dehydrated and degassed before use. IR: Nujol mulls between KBr disks, Bruker spectrophotometer type VECTOR 22. ^1H, ^{13}C, and ^{31}P NMR spectra (400, 100.6, and 162.0 MHz, respectively) were recorded with a Bruker AVANCE-400 spectrometer. For C, H, N analyses an automatic Elementar Vario ELIII analyzer was used.

Synthesis of 1. A solution of 1.07 g (2.83 mmol) of $CoMe(PMe_3)_4$ in 60 mL of pentane was combined with a solution of *N*,*N*′-bis(2,6-difluorobenzylidene)hydrazine 0.79 g (2.82 mmol) in pentane (20 mL) at −80 °C. The reaction mixture was allowed to warm to ambient temperature and stirred for 18 h. During this period, the reaction mixture turned red-brown in color. After filtering, the red solid residue was extracted with pentane (80 mL) and diethyl ether (80 mL), respectively. Repeated recrystallization from pentane at 4 °C yielded red single crystals suitable for X-ray structure analysis: 0.62 g (43.5%). Anal. Calcd for $C_{21}H_{29}CoF_4N_2P_2$ (506.3 g/mol): C, 49.82; H, 5.77; N, 5.53. Found: C, 49.78; H, 5.80; N, 5.57. IR (Nujol): 1622.5, 1607.1 (C=N), 1591.6, 1554.5 (C=C), 950.0 (PMe_3) cm^{-1}. Dec > 200 °C. ^1H NMR (400 MHz, d_8-THF, 296 K): δ 0.64 (m, 3H, CH_3), 0.94 (s, 18H, PCH_3), 6.50−7.44 (m, 6H, Ar-*H*), 9.11(s, 1H, C1*H*=N1), 10.75 (d, $^4J(HF) = 33$ Hz, 1H, C8*H*=N2). ^{13}C NMR (100.6 MHz, C_6D_6, 300 K): δ 10.2 (t, $|^1J(PC) + {}^3J(PC)| = 12.2$ Hz), 105.8 (d, $J(CF) = 19$ Hz), 111.3 (d, $J(CF) = 24.2$ Hz), 129.9 s, 130.9 s, 134.2 s, 158.9 s, 159.4 s, 159.8 s, 160.3 s, 162.4 s, Ar; 162.9 s, 163.1 s, CH=N. ^{31}P NMR (162.0 MHz, C_6D_6, 300 K): δ 8.0 (s).

Synthesis of 2. A solution of 2,6-difluorobenzonitrile (0.65 g, 4.68 mmol) in 10 mL of pentane was combined with a solution of $Co(PMe_3)_4$ (1.68 g, 4.63 mmol) in pentane (50 mL) at −80 °C. This was allowed to warm to 20 °C and stirred for 18 h to form a red-brown, turbid mixture, which was filtered. Crystallization from pentane at 4 °C yielded red-brown single crystals suitable for X-ray analysis: 1.05 g (53.3%). Anal. Calcd for $C_{16}H_{30}CoF_2NP_3$ (426.2 g/mol): C, 64.08; H, 8.34; N, 5.15. Found: C, 64.12; H, 8.30; N, 5.17. IR (Nujol): 2073.5 (C≡N), 1586.6, 1549.1 (C=C), 944.5 (PMe_3) cm^{-1}. Dec > 134 °C.

Crystallographic Data for 1. $C_{21}H_{29}CoF_4N_2P_2$, $M_r = 506.3$, crystal dimensions: 0.35 × 0.30 × 0.20 mm, monoclinic, space group $P2(1)/n$, $a = 15.3364(6)$ Å, $b = 9.0040(4)$ Å, $c = 18.6087(7)$ Å, $\beta = 109.258(1)°$, $V = 2425.86(17)$ Å^3, $T = 298(2)$ K, $Z = 4$, $D_c = 1.386$ g cm^{-3}, $\mu = 0.888$ mm^{-1}. Bruker AXS SMART APEX. A total of 29 413 reflections were collected, 5956 unique ($R_{int} = 0.0448$), $\theta_{max} = 28.20°$, multiscan absorption correction. R1 = 0.0433 (for 5956 reflections with $I > 2\sigma(I)$), wR2 = 0.1137 (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic.

Crystallographic Data for 2. $C_{16}H_{30}CoF_2NP_3$, $M_r = 426.2$, crystal dimensions: 0.20 × 0.16 × 0.14 mm, monoclinic, space group $P2(1)/n$, $a = 12.900(3)$ Å, $b = 11.552(3)$ Å, $c = 14.968(3)$ Å, $\beta = 100.001(4)°$, $V = 2196.5(8)$ Å^3, $T = 294(2)$ K, $Z = 4$, $D_c = 1.289$ g cm^{-3}, $\mu = 1.013$ mm^{-1}. A total of 12 118 reflections were collected, 4477 unique ($R_{int} = 0.0376$), $\theta_{max} = 26.39°$, semiempirical absorption correction. R1 = 0.0345 (for 4477 reflections with $I > 2\sigma(I)$), wR2 = 0.0873 (all data). The structure was solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic. CCDC-600895 and CCDC-600787 (**1** and **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Tables containing full X-ray crystallographic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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